



Structure and electrochemical properties of composite polymer electrolyte based on poly vinylidene fluoride–hexafluoropropylene/titania–poly(methyl methacrylate) for lithium-ion batteries

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HIGHLIGHTS

- Titania–PMMA organic/inorganic hybrid is synthesized via in situ polymerization.
- The hybrid increases the porosity, uptake efficiency of the PVdF–HFP membrane.
- The hybrid increases the ionic conductivity of the PVdF–HFP based CPE.
- The hybrid enhances the performance of LiCoO₂ cycled between 4.4 and 2.75 V.

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ABSTRACT

Titania–poly(methyl methacrylate) (PMMA) organic–inorganic hybrid material is synthesized via in situ polymerization. The hybrid material is employed to prepare poly vinylidene fluoride–hexafluoropropylene (PVdF–HFP) composite polymer electrolyte. The effect of the hybrid material is investigated by SEM, TG-DSC, AC impedance and charge/discharge cycling tests. The results demonstrate that the inorganic–organic hybrid material as additive increases the porosity, pore size and electrolyte uptake of the PVdF–HFP composite polymer electrolyte membrane, so that the ionic conductivity of the composite polymer electrolyte membrane is improved. The performance enhancement of the composite polymer electrolyte is confirmed by an electrochemical test using LiCoO₂/Li cells in the voltage range of 2.75–4.4 V. This study shows that titania–PMMA hybrid material is a promising additive for PVdF–HFP composite polymer electrolyte for Li-ion batteries.

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1. Introduction

With the increasing safety demands on the lithium-ion battery, more and more attention is paid to polymer electrolytes. Due to the fact that they have superior performance compared to traditional

liquid electrolytes in terms of no-leakage, high flexibility to cell geometry and high physical and chemical stability, polymer electrolytes are widely regarded as promising electrolytes for advanced Li-ion battery [1–3]. Gel polymer electrolyte (GPE) has been used in Li-ion batteries because it can provide higher ionic conductivity of about 10^{-3} S cm⁻¹ compared to the solid state polymer electrolyte [4–8]. However, the mechanical properties and electrode/electrolyte interfacial stability of GPE need to be further improved to make it extensively applicable in Li-ion battery [9,10].

Because it has excellent chemical stability and plasticity [11–14], poly(vinylidene fluoride–co-hexa-fluoropropylene) (PVdF–HFP) is considered as a promising candidate polymer matrix material for polymer electrolyte. Nano-sized ceramic fillers added into PVdF–

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HFP casting solution improve not only the mechanical properties, but also the ionic conductivity and interfacial properties between composite polymer electrolyte and electrode [15–18]. However, as a result of high surface energy of the inorganic nanoparticles, it is very difficult to disperse nanoparticles into polymer solution. Moreover, the aggregated nano-particles will negate any benefits associated with the nano scale dimension [19,20]. Valeriy V. Ginzburg [20] revealed that nanoparticle-rich phase would segregate from the polymer even at very low particle concentrations regardless of the polymer composition because of the role of strong entropic surface tension. Kim et al. [21] reported that TiO_2 nanoparticles cannot be well dispersed, even under conditions such as ultra-sonication and the subsequent ball-milling. Therefore, the main issue in obtaining an applicable inorganic/polymer composite electrolyte may be how to improve the interface compatibility between polymers and inorganic nanoparticles.

In this study, an organic/inorganic hybrid material is designed to improve the compatibility of titania with PVdF–HFP. In detail, poly(methyl methacrylate) (PMMA) is grafted onto the surface of titania particles by in-situ polymerization with vinyl triethoxy silane as coupling agent to form titanium–PMMA hybrid. Then a composite polymer electrolyte that composed of PVdF–HFP matrix and titanium–PMMA additive is successfully prepared via phase inversion. The influences of titanium–PMMA hybrid material on the pore structure of the porous membrane, and the electrochemical performance of PVdF–HFP composite polymer electrolyte-casted PE separator used in 4.4 V LiCoO_2/Li cells are investigated by SEM, TG-DSC and AC impedance, etc.

2. Experimental

2.1. Material and its pretreatment

(PVdF–HFP) is commercial fluoro-copolymer KynarFlex 2801 (Atofina Chemicals, 12 mol% HFP). Analytical grade *N,N*-dimethyl formamide (DMF) is used as solvent. Tetrabutyl titanate (TBOT) is used as the starting material to prepare titania sol by hydrolysis. Methyl methacrylate (MMA) is washed with 5 wt% NaOH solution before it is used to remove the inhibitors. Benzoyl peroxide, as initiator, is purchased from Tianjin Fuchen Chemical in China.

2.2. In situ preparation of titania–PMMA organic–inorganic hybrid material

10 mL TBOT is mixed with 50 mL ethanol to prepare “A” solution. A certain amount of deionized water is added into another 50 mL ethanol to prepare “B” solution, in which the pH of “B” solution is adjusted to 3–4 by using concentrated nitric acid. Then the “A” and “B” solution are mixed together to make a mixture in which the mole ratio of Ti to H_2O is around 1:4. The obtained mixture is then hydrolyzed at 65 °C to form titania sol. After that, vinyl triethoxy silane and MMA monomer are added into the titania sol one by one at 80 °C and polymerizes with benzoyl peroxide, as initiator. It should be mentioned that PMMA is grafted onto sol nano-titanium oxide particle surface under the effect of coupling agent vinyl triethoxy silane. The hydrolyzed vinyl triethoxy silane contains more groups of $-\text{Si}(\text{OH})_2$ and $-\text{C}=\text{C}-$, and $-\text{Si}(\text{OH})_2$ can react with $-\text{Ti}(\text{OH})_4$ to form $-\text{Si}(\text{O}-\text{Ti})_3$, then $-\text{C}=\text{C}-$ can be polymerized with MMA monomer to form in situ sol–gel nano-titanium oxide/PMMA hybrid material.

2.3. Preparation of sandwich type porous membranes

PE separator is used as supporting membrane [22], and PVdF–HFP based porous membranes are fixed to both sides of it. The

procedure is as follows: First, pristine PVdF–HFP or PVdF–HFP with titania–PMMA hybrid additive (10 wt%) is dissolved in *N,N*-dimethyl formamide (DMF) to form a homogenous solution, with concentration of 15 wt%. Then the solution is casted on both sides of PE separator to form sandwich-type film at room temperature. After casting, the sandwich-type composite membranes are submerged into distilled water bath immediately. The characterization of the sandwich porous membranes is carried out after further submerged in absolute alcohol for 2 h and then dried in vacuum oven at 60 °C for 2 days. The dry thickness of the resulting membranes is about 40 μm .

2.4. Sample characterization

The chemical species of the titania–PMMA hybrid material is examined by FT-IR (Jasco Co., FT-IR470). The structure and morphology of porous membranes are analyzed by a scanning electron microscope (SEM, JSM6301F) with an accelerating voltage of 20 kV. Thermal analysis is performed using Q2000 TA Instruments, under nitrogen atmosphere in a temperature range from 30 to 400 °C with a heating rate of 10 °C min^{−1}.

Liquid uptake is measured by weighting method. The dry pristine PVdF–HFP or PVdF–HFP and Titania–PMMA blends composite membranes are cut into identical round pieces. After being carefully dried and weighted, the pieces are submerged in propylene carbonate (PC). After a certain period of time (5 min), the fully swelling pieces are taken out, and the excess liquid is sucked away by filter papers. Then the pieces are weighted, and the liquid uptake is calculated using the following formula [23]:

$$\text{Membrane liquid uptake} = \frac{w_t - w_0}{w_0} \times 100\%$$

where w_0 is the weight of the dry piece, w_t is the weight of the piece after fully swelling. In this paper, liquid uptake is the mean value of 5 parallel samples.

2.5. Electrochemical measurement

As-prepared composite membranes are cut into identical round pieces, then submerged in the liquid electrolyte, which is prepared by 1.0 M LiPF_6 dissolving in 1:1 (v/v) mixture of ethylene carbonate (EC) and diethylene carbonate (DEC), to form composite polymer electrolyte. Ionic conductivity of the composite polymer electrolytes are tested by AC impedance technique [11] in the frequency range from 1 Hz to 1 MHz and at different temperatures (−5, 5, 15, 25, 35, 45, 55, 65 °C). A thermostatic bath with ± 0.1 °C precision is utilized to precisely control the temperature.

The test of the LiCoO_2/Li 2032-type coin cell is performed galvanostatically at room temperature at charge–discharge rate 0.5 C in the voltage range of 2.75–4.4 V using Land Battery Test System (Wuhan Land Electronic Co. Ltd) [24,25]. The cathode consists of 85 wt% LiCoO_2 (Shanshan Co. Ltd), 10 wt% carbon black, and 5 wt% binder. The cell assembly is carried out in an argon filled glove box, with oxygen content less than 2 ppm and H_2O content less than 1 ppm.

3. Results and discussion

The FTIR spectra of vinyl triethoxy silane, titania sol, and titania–PMMA hybrid material are shown in Fig. 1(A), (B) and (C), respectively. Titania is confirmed by $-\text{Ti}(\text{O})_4-\text{Ti}-$ absorption band at 500–720 cm^{-1} [26–28]. The characteristic absorption peaks of vinyl triethoxy silane, which are 1295, 1276, 1106 and 1082 cm^{-1} , appeared in the spectrum of titania–PMMA hybrid material but

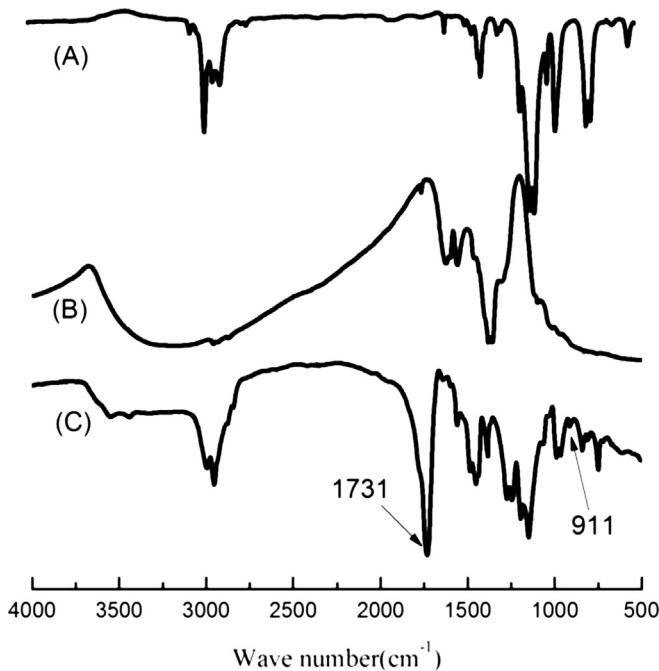


Fig. 1. FTIR spectra of (A) vinyl triethoxy silane, (B) titania, and (C) titania–PMMA hybrid.

shifted to 1273, 1244, 1194, 1148 cm^{-1} , and the peak in the region 911 cm^{-1} was assigned to the stretching vibration band of $-\text{Si}=\text{O}-\text{Ti}-$ [29,30]. Those results indicate that because of the formation of $\text{Si}=\text{O}-\text{Ti}$, vinyl triethoxy silane is grafted onto titania particles. The peak that appears at 1731 cm^{-1} [31,32] can be attributed to the stretching mode of carbonyl group, and it indicates that PMMA is successfully grafted onto titania sol as well.

The dispersity of titania–PMMA organic–inorganic hybrid material in PVdF–HFP casting solution can be well evaluated according to Tyndall scattering. It is well known that, when nano-sized particles are dispersed in a solution, a laser beam going through the dispersion can give evidence whether the nanoparticles have a good dispersibility in the solution or not. As shown in Fig. 2, pristine PVdF–HFP dissolved in DMF (Fig. 2A) results in colorless transparent solution. In contrast, it turned to pale blue transparent solution after the hybrid material was added in (Fig. 2B), as well as a red laser beam of Tyndall scattering. The Tyndall scattering test indicates that as a result of high compatibility between PMMA and

DMF, titania–PMMA hybrid materials disperse well in PVdF–HFP solution.

Fig. 3 shows the SEM images of a surface of the composite PE separator. During the film-casting process, mutual diffusion promptly occurs between solvent and non-solvent to make highly porous structures in polymer matrix, and the content and property of the additive in casting solution affects the size and number of pores [21]. Compared to the pristine PVdF–HFP membrane, the blends composite membrane has larger pores (~ 500 nm), and the pores are more closely and evenly distributed. Those results show that the organic–inorganic hybrid material has a strong influence on size and distribution of pores. Since the PMMA grafted in the hybrid material is a kind of oligomer, which can easily make micro phase separation in PVdF–HFP matrix, a large quantity of micro porous is produced during the procedure of wetting–film gelation. Because adding the hybrid material into PVdF–HFP casting solution favors the creation and growth of the pores, the blends-casted PE separator has more pores and larger pore size.

Fig. 4 shows the TG curves of titania–PMMA hybrid material, pristine PVdF–HFP membrane and the blends composite membrane. Pristine PVdF–HFP membrane is inferior to the blends composite membrane in terms of thermal stability, as the decomposition temperature of the two samples is 350 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$ respectively. The blend suffers less decomposition even when the test temperature reaches 320 $^{\circ}\text{C}$ and the thermal stability of it under 320 $^{\circ}\text{C}$ can well meet the thermal safety requirement of lithium ion battery.

Fig. 5 shows the DSC curves of titania–PMMA hybrid material, pristine PVdF–HFP membrane and the blends composite membrane. Pristine PVdF–HFP membrane shows a characteristic endothermic peak at 139.4 and 166.5 $^{\circ}\text{C}$, which corresponds to the melting temperature (T_m) of PVdF–HFP porous layer and PE support layer due to the crystalline difference, respectively. For the blends composite membrane, T_m of PVdF–HFP based porous layer and supports PE layer is increased to 142.3 and 172.5 $^{\circ}\text{C}$, respectively. Similar results were obtained in some reports [15,17], which concluded that the ceramics particles lead to obvious increase in T_m of the membrane matrix.

The polymer membrane with higher porosity is suitable for holding larger amounts of liquid electrolyte, so that can achieve higher ionic conductivity at room temperature [33]. As shown in Fig. 6, pristine PVdF–HFP membrane has a lower liquid uptake than the blends membrane; the saturation value of pristine PVdF–HFP membrane is about 130%, while that of the blends is 200%. That result is consistent with SEM analysis (Fig. 3), in which the higher pore size and distribution density, the more liquid uptake. As a result it takes only 5 min for the blend based sandwich-type porous

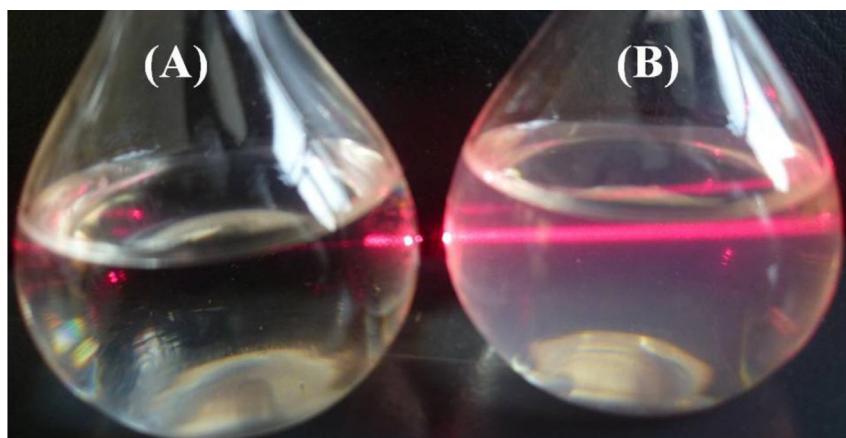


Fig. 2. The photos of (A) pristine PVdF–HFP and (B) PVdF–HFP and titania–PMMA (10 wt%) blends in DMF.

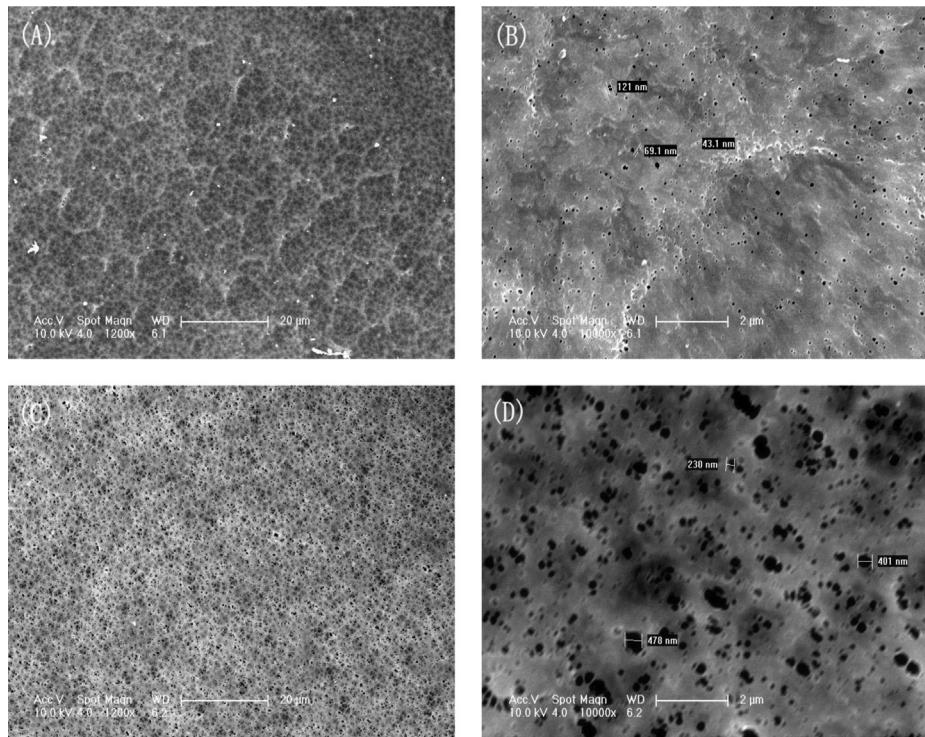


Fig. 3. The SEM images of the surface for (A) $\times 1200$, (B) $\times 10,000$ pristine PVdF–HFP membrane and (C) $\times 1200$, (D) $\times 10,000$ PVdF–HFP and titania–PMMA blends composite membrane.

membrane in PC to reach its maximum uptake. Therefore, it can be deduced that fully interconnected pore channels are produced by phase inversion process so that it's easy to be swelled by liquid electrolyte [17,23].

The ionic conductivity of PVdF–HFP/titania–PMMA blends composite polymer electrolyte is tested to be about $3.4 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature (25°C), while it is $1.9 \times 10^{-3} \text{ S cm}^{-1}$ for pristine PVdF–HFP gel polymer electrolyte. Even at the condition of -5°C , the ionic conductivities of the blends composite polymer electrolyte is still above $10^{-3} \text{ S cm}^{-1}$. The values

are rather acceptable for Li-ion battery application. Comparing Figs. 6 and 7, it can be observed that higher uptake leads to higher ionic conductivity. Furthermore, the higher ionic conductivity is related to not only the liquid uptake, but also the location of titania–PMMA on internal surface of pores channel, because it can create favorable Lithium ionic conduction pathway in their vicinity or through Lewis acid–base interaction [34–36].

The charge capacity of a 4.4 V LiCoO_2 battery is about 12% greater than that of a 4.2 V LiCoO_2 battery. However, because of the reaction between the overcharged cathode and electrolyte [24,25],

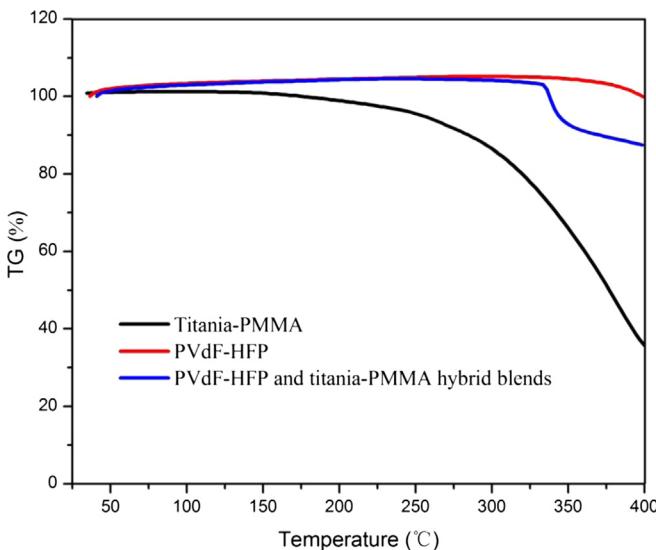


Fig. 4. TG curves of titania–PMMA hybrid material, pristine PVdF–HFP and their blends porous membranes.

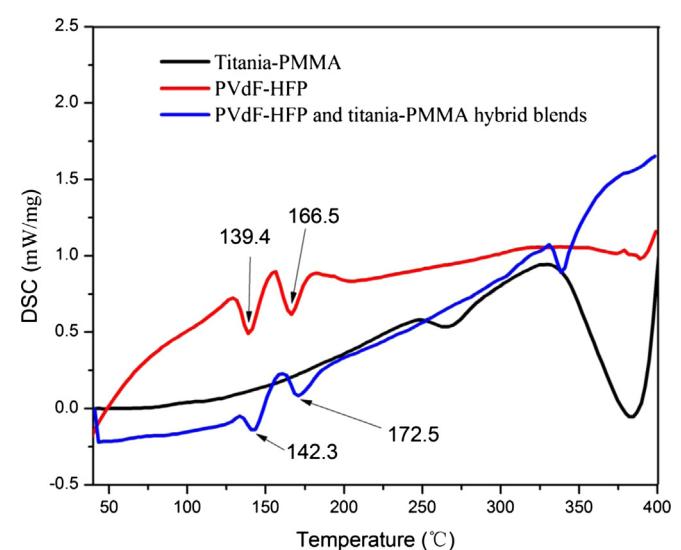


Fig. 5. DSC curves of titania–PMMA hybrid, pristine PVdF–HFP and their blends porous membranes.

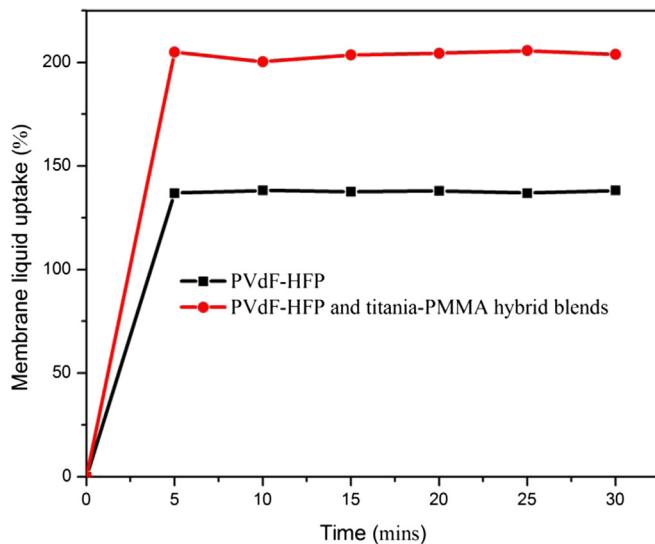


Fig. 6. PC uptake of the PVdF–HFP based porous membranes with and without titania–PMMA hybrid.

overcharge generally leads to capacity fade in a battery. Fig. 8 shows the charge–discharge cycling performance of LiCoO_2/Li button cells with different electrolytes (0.5 C rate, in the voltage range of 2.75–4.4 V, room temperature). The cell with PVdF–HFP/titania–PMMA blends composite polymer electrolyte has better cyclic performance than that with liquid electrolyte and pristine PVdF–HFP gel polymer electrolyte. All of the three cells show typical voltage plateau during the first cycle and show high discharge capacities of around 168 m Ah g^{-1} , as shown in Fig. 9. However, after 50 cycles, the capacity of the cell with liquid electrolyte is dropped to $144.5 \text{ m Ah g}^{-1}$, while the cell with pristine PVdF–HFP GPE and blend CPE presents a capacity of $155.6 \text{ m Ah g}^{-1}$ and $160.4 \text{ m Ah g}^{-1}$ respectively. Especially after 100 cycles, the capacity retention is found to be 42% for the liquid electrolyte cell, 76% for pristine PVdF–HFP GPE cell and 87% for the blend CPE cell. Those results confirm that titania–PMMA hybrid material that dispersed in PVdF–HFP porous membrane hinders the reaction between LiCoO_2

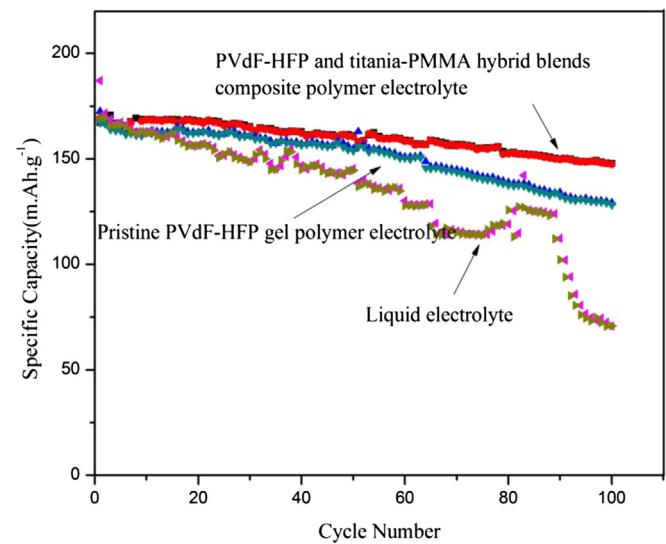


Fig. 8. Charge–discharge cycling of the LiCoO_2/Li cells using different electrolytes (cut-off voltage 2.75–4.4 V, 0.5 C rate current, room temperature).

and electrolyte greatly, which in return retards the capacity fading of LiCoO_2 .

4. Conclusion

Titania–PMMA organic–inorganic hybrid material can be successfully prepared by in-situ polymerization and can be well

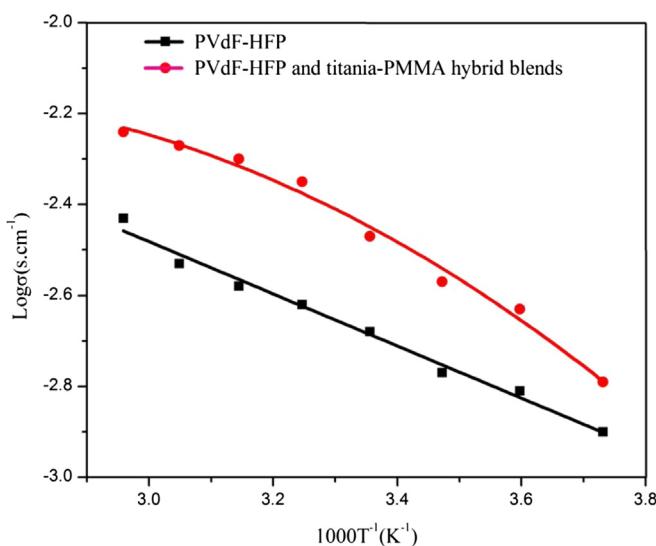


Fig. 7. Arrhenius plots for the ionic conductivities of PVdF–HFP based composite polymer electrolyte with or without titania–PMMA hybrid.

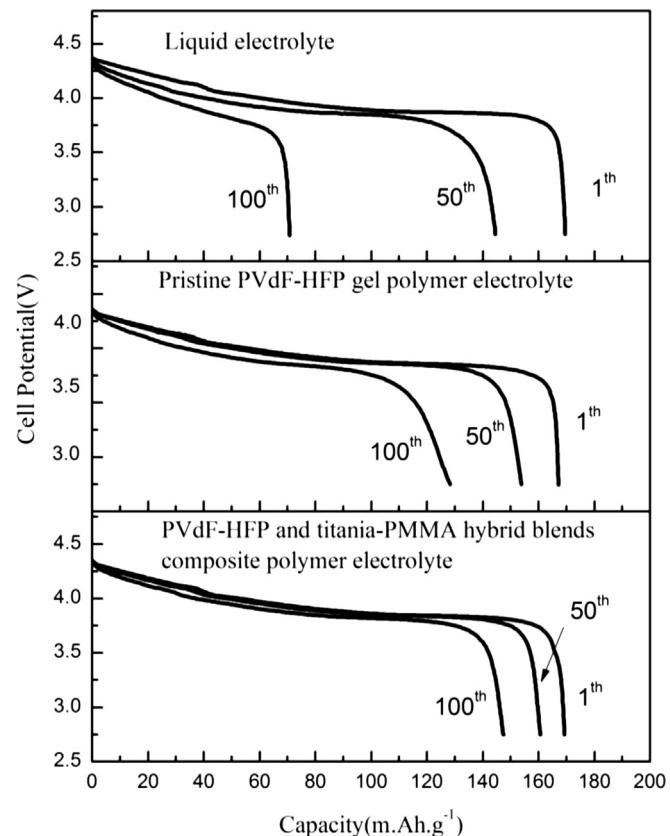


Fig. 9. Discharge profiles of the LiCoO_2/Li cells with different electrolyte (cut-off voltage 2.75–4.4 V, 0.5 C rate current, room temperature).

dispersed in PVdF–HFP casting solution. Sandwich-type membranes, consisting of PVdF–HFP based porous layer and PE supporting layer, can be then prepared by the phase inversion. Titania–PMMA hybrid material as additive shows improvement of the property of PVdF–HFP polymer electrolyte membrane in terms of pore size, pore distribution and electrolyte uptake, so that the ionic conductivity of the composite electrolyte is increased. The ionic conductivity of PVdF–HFP/titania–PMMA blends composite polymer electrolyte is about 3.4×10^{-3} S cm $^{-1}$ at room temperature (25 °C). The composite separator suffers only little decomposition even when the test temperature reaches 350 °C, and TG-DSC analysis shows it has a good thermal stability. Moreover, the blend membrane exhibits high charge–discharge performance even at high cut-off voltage of 4.4 V. The results demonstrate that the proposed titania–PMMA organic–inorganic hybrid material is a promising additive for PVdF–HFP composite polymer electrolyte that can be used in Lithium-ion batteries.

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